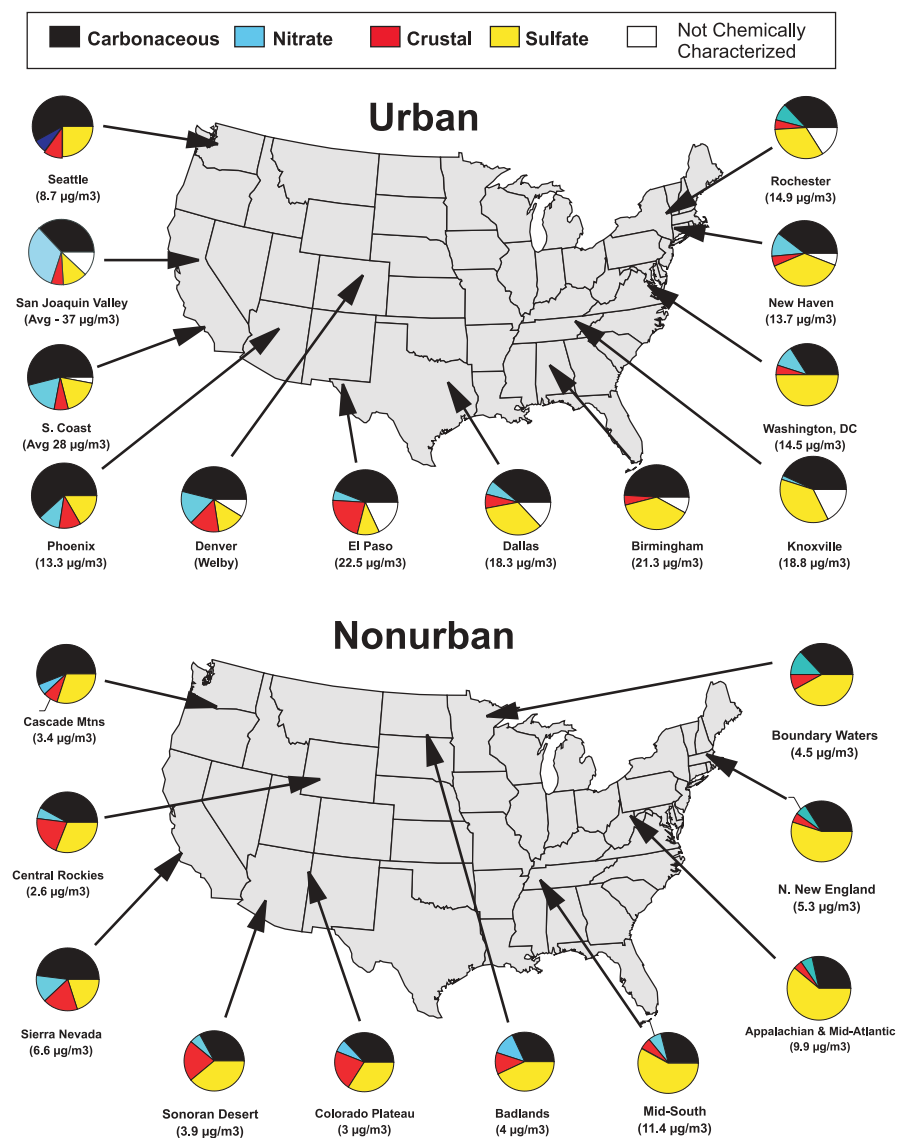


nitrogen oxides, carbonaceous and crustal-related particles. SO_2 is emitted mostly from the combustion of fossil fuels in boilers operated by electric utilities and industry. Less than 20 percent of SO_2 emissions nationwide are from other sources, mainly industrial processes and mobile sources. NO_x emissions are more evenly divided between stationary source and onroad mobile source fuel combustion, accounting for almost 80 percent of SO_2 emissions. Nonroad mobile sources account for most of the remaining emissions. SO_2 and NO_x combine with ammonia in the atmosphere under certain conditions to form ammonium sulfate and nitrate particles. Animal husbandry, mobile sources, fertilizer application and industrial processes are the main sources of ammonia, with animal husbandry contributing about 80 percent of the emissions. The main sources of carbonaceous particles are biomass and fossil fuel combustion with the open burning of biomass accounting for about one-third of the carbonaceous material emissions. Other important categories are mobile sources, various industrial processes, residential wood stoves and fireplaces, and organic soils and plant materials. Principal mobile sources include both on and off road diesels, gasoline engines, aircraft, railroads, and ships. The main sources of crustal particles are roads, construction and agriculture, but as discussed earlier, some of the crustal materials reported in Figures 2-55 and 2-56 come from combustion emissions. High wind events also can contribute large quantities of crustal materials to the air. However, since wind events are of relatively short duration, they are not included in annual emission estimates such as the NEI. While

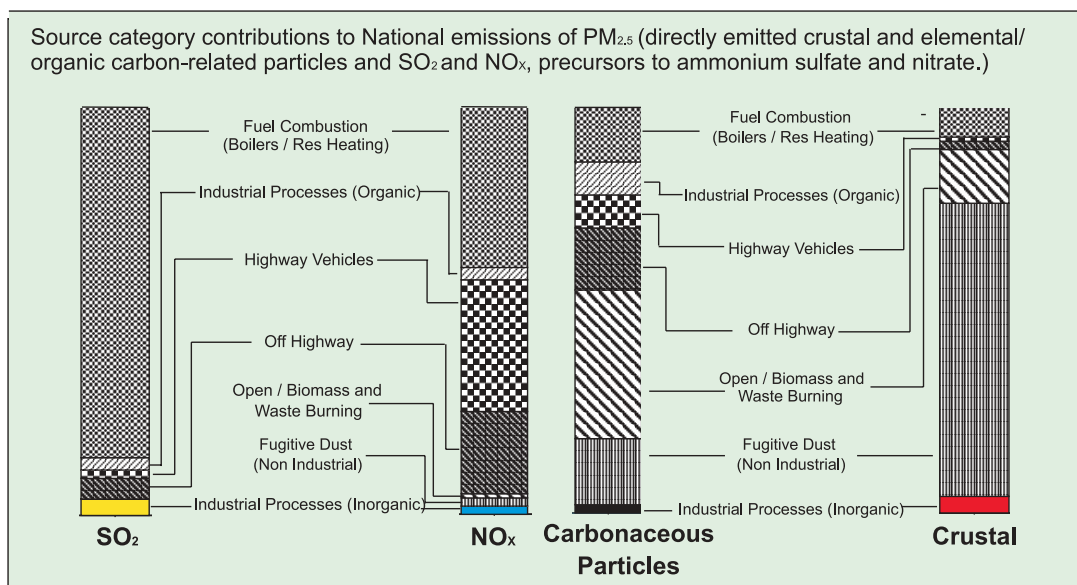
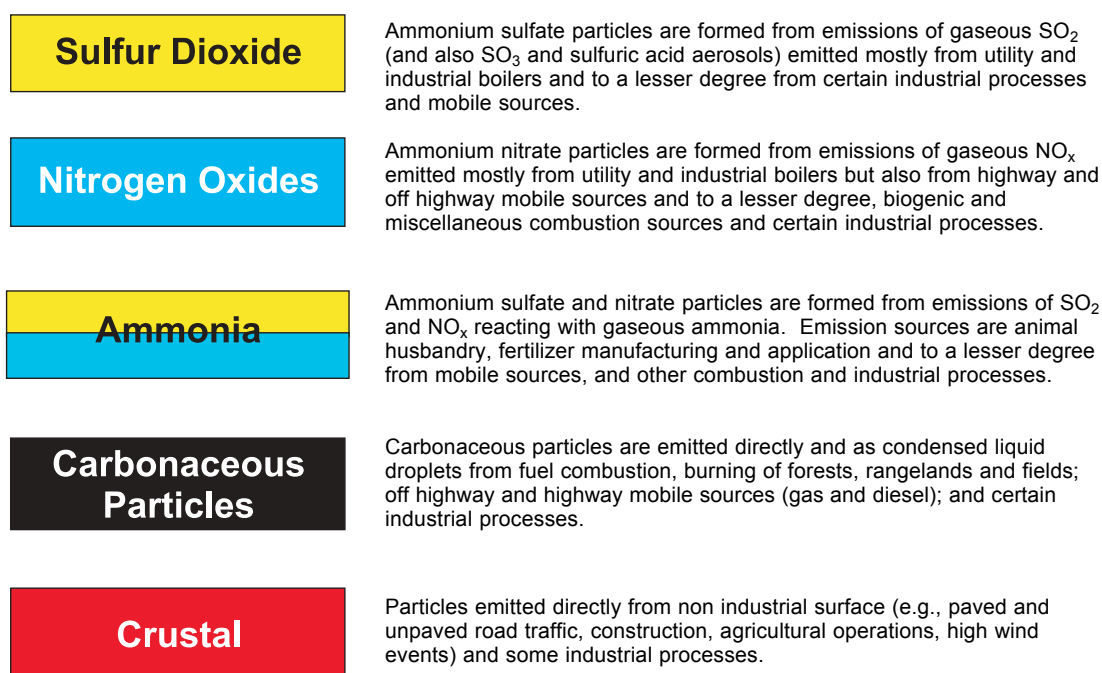
Figure 2-55. $\text{PM}_{2.5}$ ambient composition.



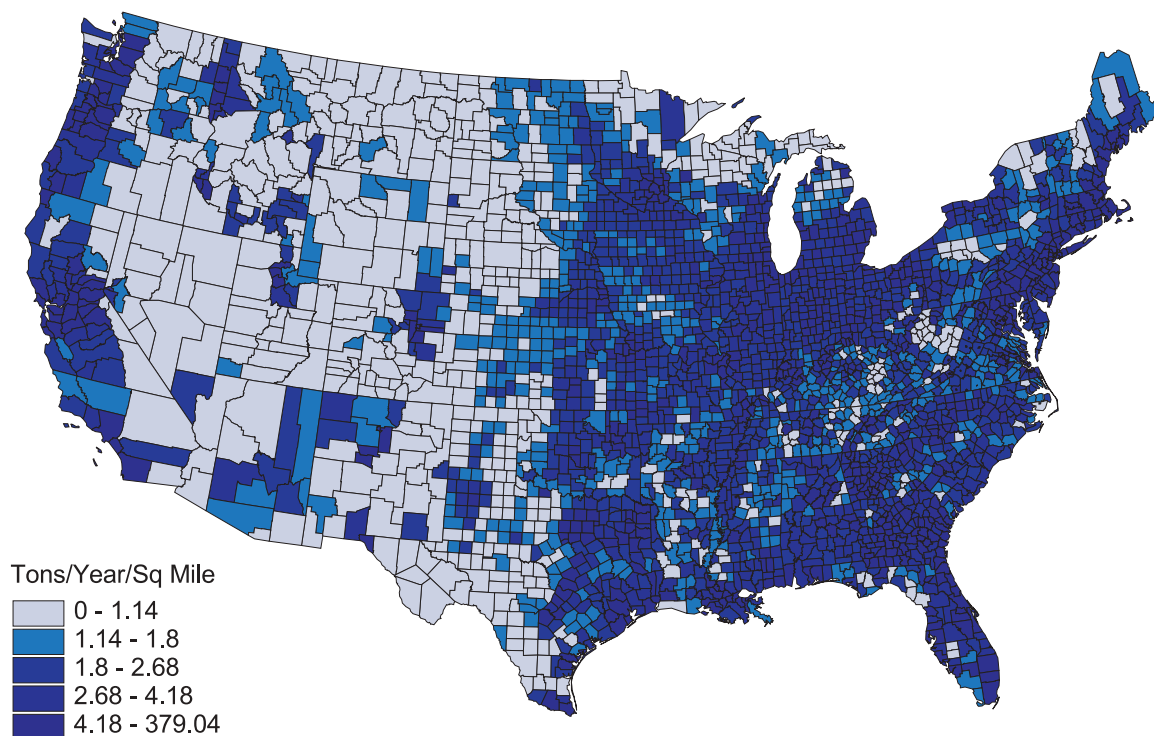
Notes:

See Appendix B for a full discussion of data sources.

$\text{PM}_{2.5}$ mass concentrations are determined using at least 1 year of monitoring at each location using a variety of sampling methods. They should not be used for comparisons to the $\text{PM}_{2.5}$ NAAQS.

Figure 2-56. PM_{2.5} emission sources.**Note:**

Composition and source contributions vary among urban areas. Also, some carbonaceous material is formed from organic gases reacting in the atmosphere. The magnitude of these "secondary" organics is believed small but more studies are needed by the research community.

Figure 2-57. Direct PM_{2.5} emissions density by county, 1999.

crustal materials are the predominant component of PM₁₀. Figure 2-56 shows that PM_{2.5} is predominantly comprised of secondary particles and directly emitted carbonaceous particles. The composition (and thus the sources) of PM_{2.5} and PM₁₀ are markedly different because most of the crustal material particles are larger than 2.5 micrometer aerodynamic diameter while almost all of the secondary particles and directly emitted carbonaceous particles are smaller than 2.5 micrometers.

Used together, Figures 2-55 and 2-56 can give a qualitative feel for the combined influence of specific source types on ambient PM_{2.5} overall (e.g., fuel combustion in boilers, organic and inorganic industrial processes, highway and off highway mobile

sources, open burning of waste/biomass and fugitive dust). For example, Figure 2-56 shows that fuel combustion in boilers contributes significantly to both sulfate and carbonaceous mass. Figure 2-57 shows that both sulfate and carbonaceous particles are found in abundance in PM_{2.5} in the east and that carbonaceous particles are also abundant in the west. Thus, one could conclude that fuel combustion in boilers is a significant contributor to PM_{2.5} in the ambient air. In contrast, one could conclude that fugitive dust sources do not play a particularly important role in ambient air samples of PM_{2.5}. It is important to note, however, that PM₁₀ crustal particles have been shown to be significant contributors to visibility impairment in the western United States.³⁴

National Trends in PM_{2.5} Emissions

Figure 2-57 shows the emission density for PM_{2.5} in each U.S. county. PM_{2.5} emission density is the highest in the eastern half of the United States, in large metropolitan areas, areas with a high concentration of agriculture such as the San Joaquin Valley in California and along the Pacific coast. This closely follows patterns in population density. One exception is that open biomass burning is an important source category that is more prevalent in forested areas and in some agricultural areas. Fugitive dust is a lower fraction of PM_{2.5} emissions than they are for PM₁₀.

Figure 2-58 shows that total direct PM_{2.5} emissions decreased 12 percent between 1990 and 1999, which is a

similar 10-year trend to that for PM_{10} . The relative source contribution to $PM_{2.5}$ versus PM_{10} is different, as shown in Figures 2-59 and 2-60. When both traditionally inventoried and miscellaneous categories are considered together, combustion sources account for a higher percentage of total emissions for $PM_{2.5}$ than for PM_{10} .

As discussed earlier, ammonia is important in explaining the formation of sulfate and nitrate. Figure 2-61 is a pie chart showing 1999 NH_3 emissions by source category. It shows that livestock (and to a lesser extent fertilizer application) are the most important NH_3 sources, accounting for 87 percent of total ammonia emissions.

Characterizing Coarse Fraction PM Air Quality

An approximation of coarse fraction PM can be obtained by subtracting $PM_{2.5}$ from PM_{10} at collocated FRM monitors. Since the protocol for each monitor is not identical, the resulting estimate should be viewed with caution. A more complete and accurate view of $PM_{10-2.5}$ values can be obtained by nationwide deployment of PM_{10} and $PM_{2.5}$ monitors that use an equivalent monitoring protocol. Figure 2-62 shows estimated annual mean $PM_{10-2.5}$ and Figure 2-63 shows the estimated 98th percentile 24-hour average $PM_{10-2.5}$ developed from 1999 FRM monitor data. The limited data show that annual mean concentrations vary widely, with higher concentrations in several areas of the Midwest and southern California. A similar pattern emerges for the estimated 98th percentile 24-hour average

Figure 2-58. National direct $PM_{2.5}$ emissions trend, 1990–1999 (traditionally inventoried sources only).

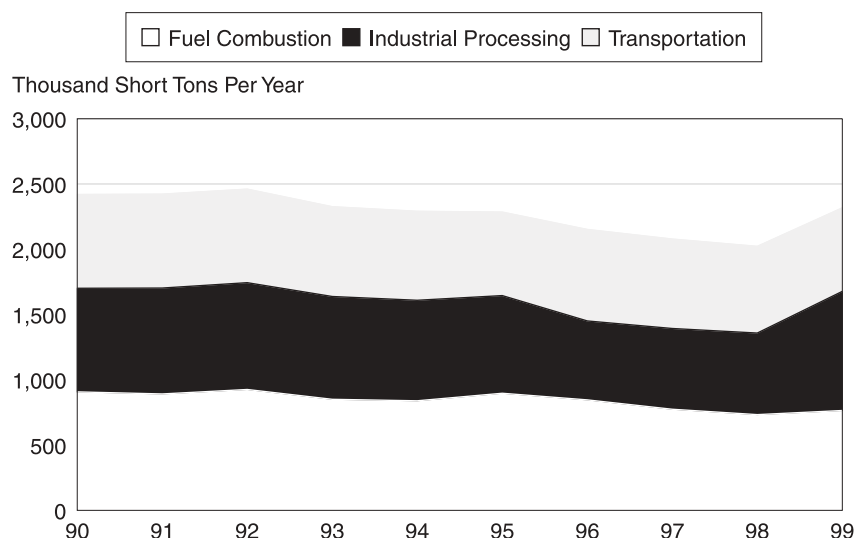


Figure 2-59. Direct $PM_{2.5}$ emissions from traditionally inventoried source categories, 1999.

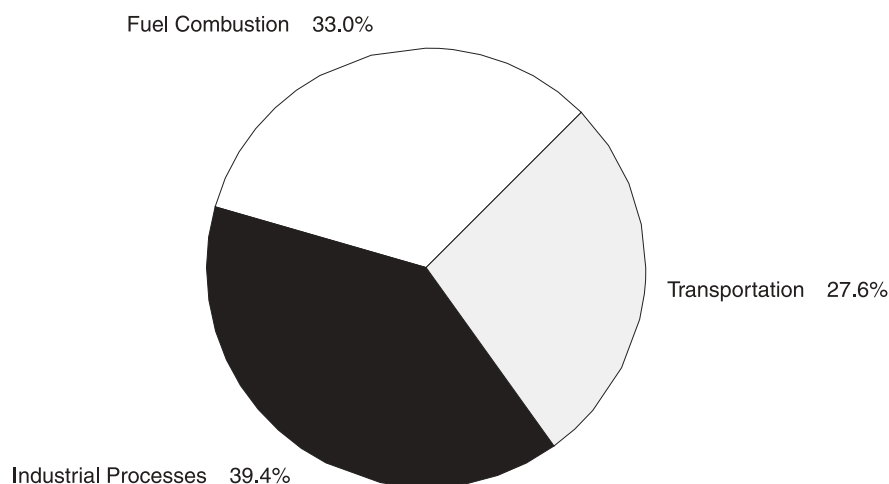
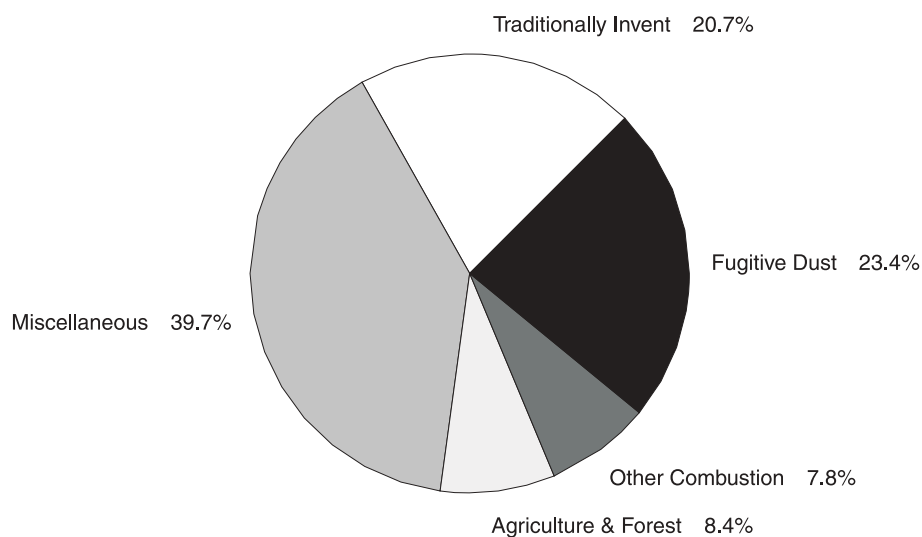


Figure 2-60. Total direct PM_{2.5} emissions by source category, 1999.

PM_{10-2.5} concentrations. Though the Southeast data is relatively incomplete, preliminary estimates suggest relatively low PM_{10-2.5} levels throughout that region.

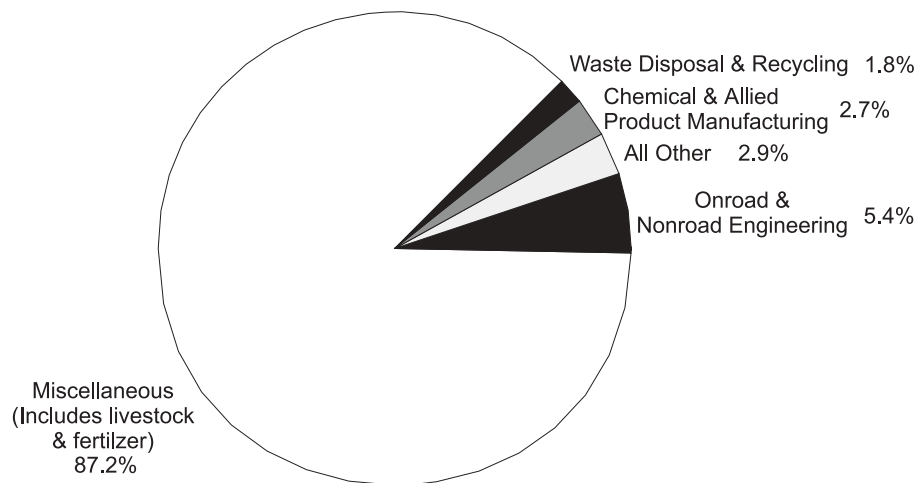
Figure 2-61. National ammonia emissions by principal source categories, 1999.

Figure 2-62. Estimated 1999 annual mean $PM_{10-2.5}$.

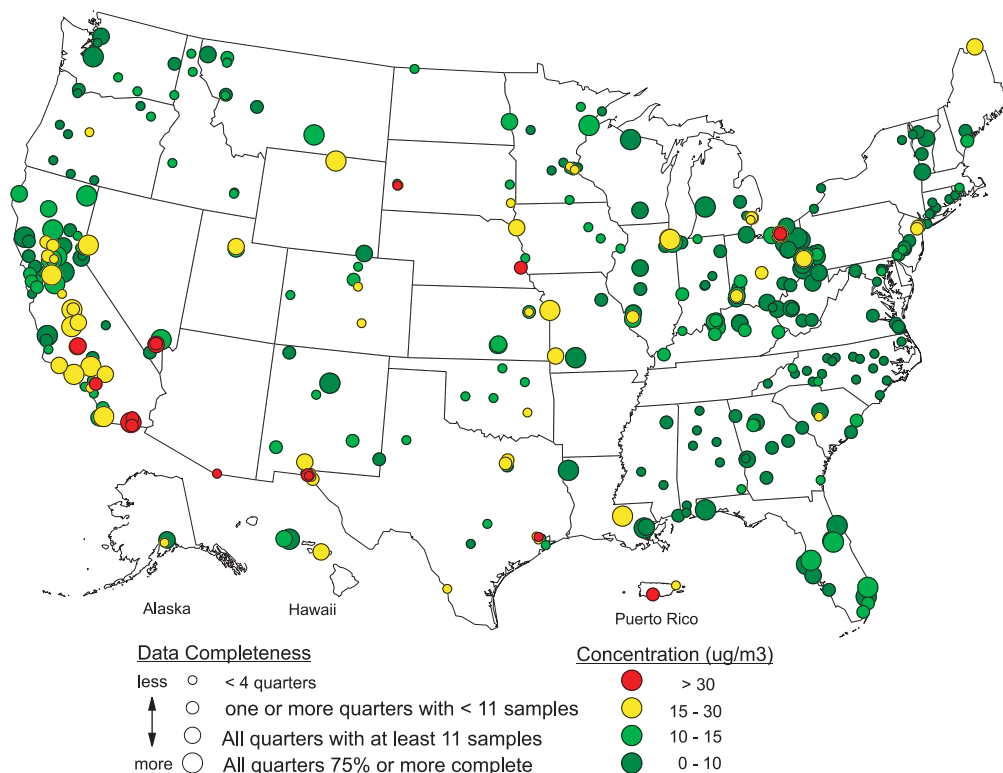
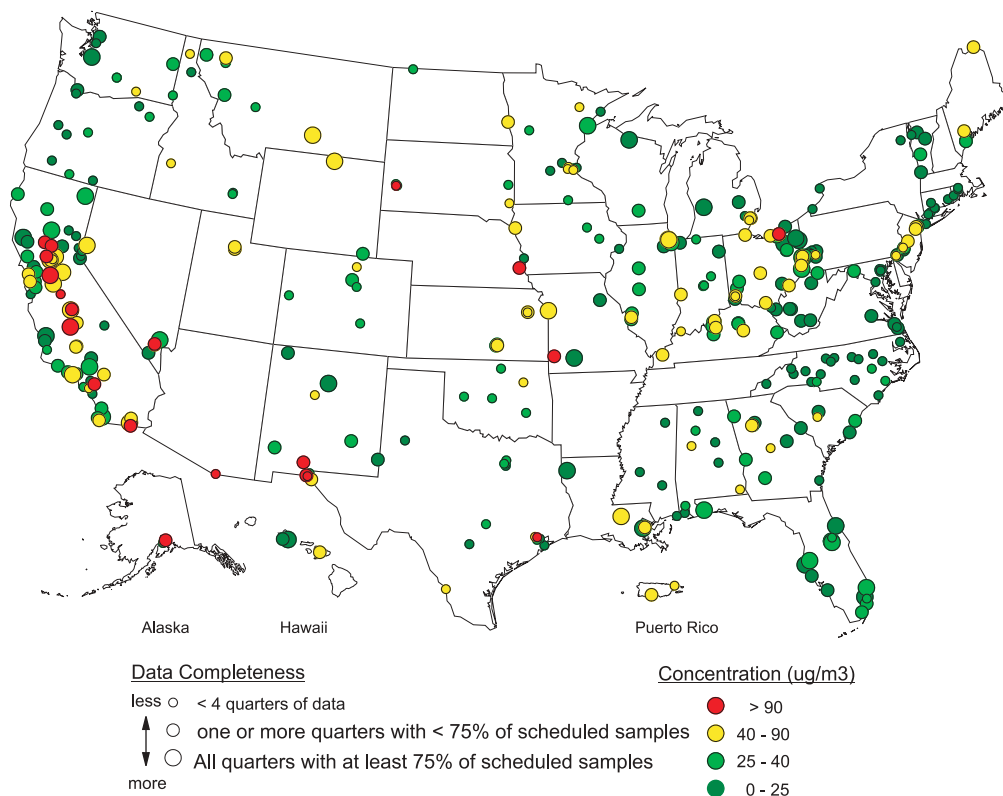


Figure 2-63. Estimated 1999 98th percentile 24-hour average $PM_{10-2.5}$ developed from 1999 FRM monitor data.



Sulfur Dioxide

Air Quality Concentrations

1980-99	50% decrease
1990-99	36% decrease
1998-99	2% decrease

Emissions

1980-99	27% decrease
1990-99	20% decrease
1998-99	3% decrease

Worth Noting:

- Steady 20-year improvement has reduced SO₂ ambient concentrations by one-half and emissions by one-third.
- Phase II of the Acid Rain Program was implemented in 2000 and should result in significant new reductions.

Nature and Sources

Sulfur dioxide (SO₂) belongs to the family of sulfur oxide (SO_x) gases. These gases are formed when fuel containing sulfur (mainly coal and oil) is burned, and during metal smelting and other industrial processes. The highest monitored concentrations of SO₂ have been recorded in the vicinity of large industrial facilities.

Health and Environmental Effects

High concentrations of SO₂ can result in temporary breathing impairment for asthmatic children and adults who are active outdoors. Short-term exposures of asthmatic individuals to elevated SO₂ levels while at moderate exertion may result in reduced lung function that may be accompanied by symptoms such as wheezing, chest tightness, or shortness of breath. Other effects that have been associated with longer-term exposures to high concentrations of SO₂, in conjunction with high levels of PM, in-

clude respiratory illness, alterations in the lungs' defenses, and aggravation of existing cardiovascular disease. The subgroups of the population that may be affected under these conditions include individuals with cardiovascular disease or chronic lung disease, as well as children and the elderly.

Additionally, there are a variety of environmental concerns associated with high concentrations of SO₂. Because SO₂, along with NO_x, is a major precursor to acidic deposition (acid rain), it contributes to the acidification of soils, lakes and streams and the associated adverse impacts on ecosystems (see Chapter 7, Atmospheric Deposition of Sulfur and Nitrogen Compounds). Sulfur dioxide exposure to vegetation can increase foliar injury, decrease plant growth and yield, and decrease the number and variety of plant species in a given community. Sulfur dioxide also is a major precursor to PM_{2.5} (aerosols), which is of significant concern to human health (as discussed in the particulate matter section of this chapter), as well as a main pollutant that impairs visibility (see Chapter 6, Visibility Trends). Finally, SO₂ can accelerate the corrosion of natural and man-made materials (e.g., concrete and limestone) which are used in buildings and monuments, as well as paper, iron-containing metals, zinc and other protective coatings.

Primary and Secondary Standards

There are both short- and long-term primary NAAQS for SO₂. The short-term (24-hour) standard of 0.14 ppm (365 µg/m³) is not to be exceeded more than once per year. The long-term standard specifies an annu-

al arithmetic mean not to exceed 0.030 ppm (80 µg/m³). The secondary NAAQS (3-hour) of 0.50 ppm (1,300 µg/m³) is not to be exceeded more than once per year. The standards for SO₂ have undergone periodic review, but the science has not warranted a change since they were established in 1972.

National 10-Year Air Quality Trends

The national composite average of SO₂ annual mean concentrations decreased 36 percent between 1990–1999 as shown in Figure 2-64, with the largest single-year reduction (16 percent) occurring between 1994 and 1995.³⁰ The composite trend has since leveled off, declining only 3 percent from 1998–1999. This same general trend is seen in Figure 2-65, which plots the ambient concentrations grouped by rural, suburban, and urban sites. It shows that the mean concentrations at the urban and suburban sites are consistently higher than those at the rural sites. However, the 1994–1995 reduction in the concentrations at non-rural sites does narrow the gap between the trends. The greater reduction seen in the non-rural sites reflects the fact that the proportion of non-rural sites is greater in the eastern United States, which is where most of the 1994–1995 emissions reductions at electric utilities occurred.³⁴ The national composite second maximum 24-hour SO₂ annual mean concentrations decreased 38 percent between 1990 and 1999, as shown in Figure 2-64 with the largest single-year reduction (25 percent) occurring between 1994 and 1995. See also Chapter 7, Atmospheric deposition of Sulfur and Nitrogen Compounds. A map of 1999 SO₂

monitor locations may be found in Figure B-6 in Appendix B.

National Emissions Trends

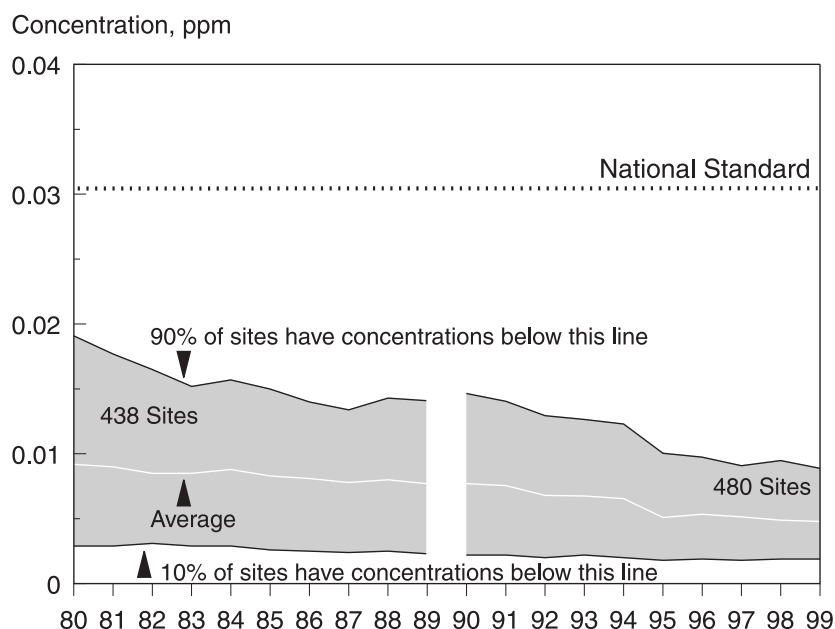
National SO₂ emissions decreased 20 percent between 1990 and 1999, with a sharp decline between 1994 and 1995, similar to the decline in the ambient concentrations. Unlike the air quality trend, however, the emissions trend remains essentially level from 1996–1999, as shown in Figure 2-66. This dramatic reduction in 1995 was caused by implementation of the Acid Rain Program; subsequent year-to-year variations are driven in part by the yearly changes in emissions from the electric utility industry. The electric utility industry accounts for most of the fuel combustion category in Figure 2-67. In particular, the coal-burning power plants have consistently been the largest contributor to SO₂ emissions, as documented in Table A-8 in Appendix A. See also Chapter 7, Atmospheric Deposition of Sulfur and Nitrogen Compounds.

The Acid Rain Program

The substantial national reductions in SO₂ emissions and ambient SO₂ and sulfate concentrations from 1994–1999) are due mainly to Phase I implementation of the Acid Rain Program. Established by EPA under Title IV of the CAAA, the Acid Rain Program's principal goal is to achieve significant reductions in SO₂ and NO_x emissions from electric utilities. Phase I compliance for SO₂ began in 1995 and significantly reduced emissions from the participating utilities.³⁵ Table 2-6 shows this reduction in terms of units required to participate in Phase I and other units.

Between 1996–1998 total SO₂ emissions from electric utilities have increased slightly, compared to 1995. In

Figure 2-64. Trend in annual mean SO₂ concentrations, 1980–1999.



Note: When the total number of rural, suburban, and urban sites are summed for either the 1980–89 or 1990–99 time periods in Figure 2-26, this number may not equal the total number of sites shown in Figure 2-25 for the same time periods. This is due to a few monitoring sites falling outside the definitions of rural, suburban, or urban sites.

Figure 2-65. Annual mean SO₂ concentration by trend location, 1980–1999.

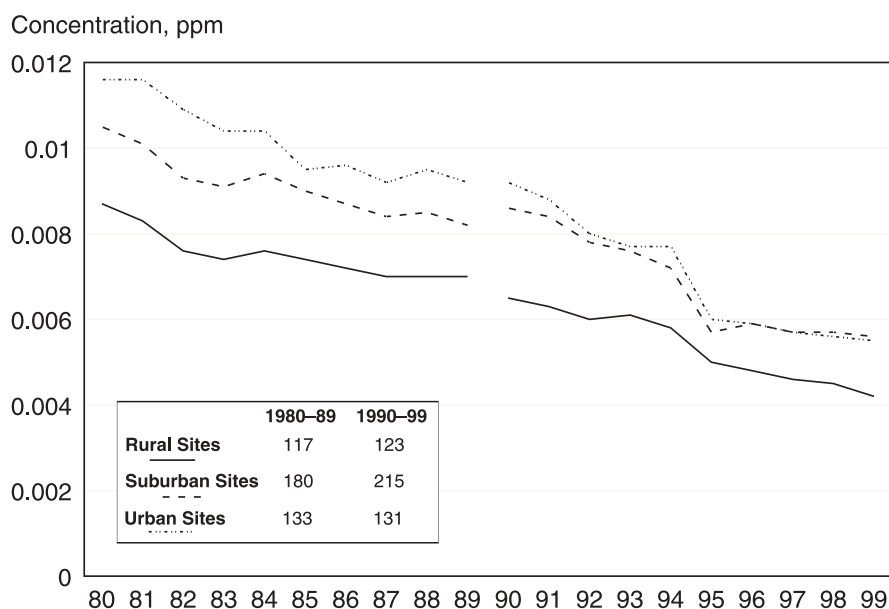
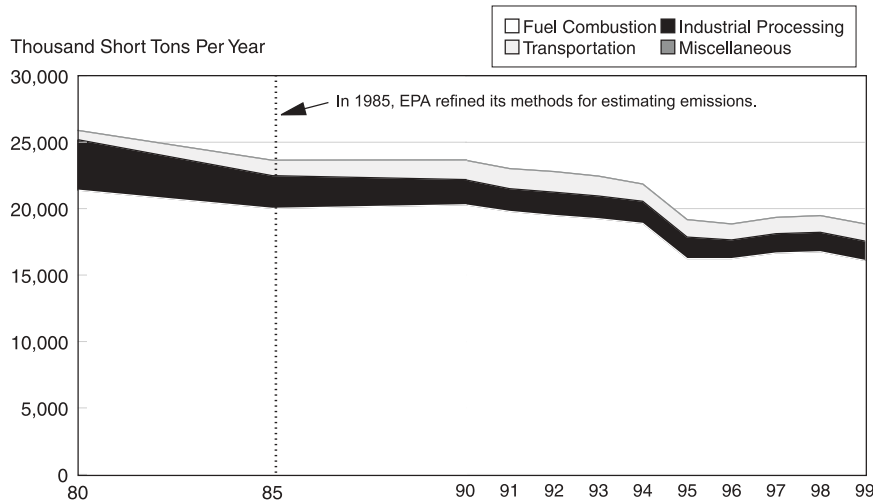
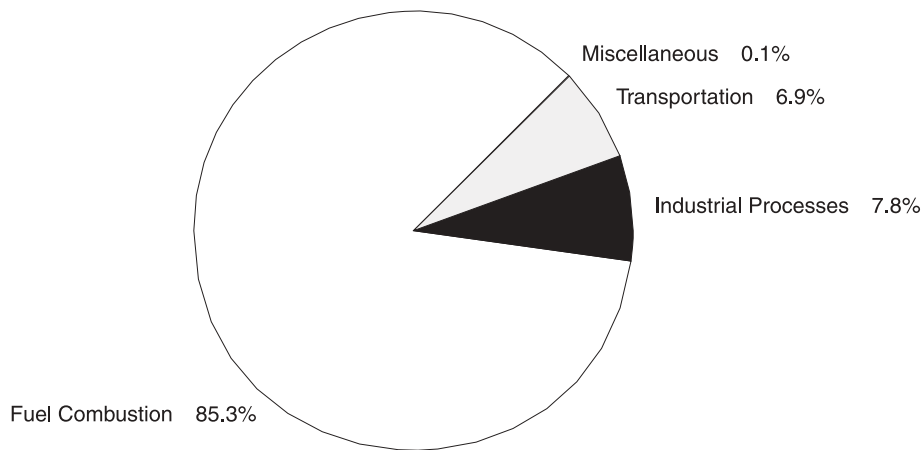


Figure 2-66. National total SO₂ emissions trend, 1980–1999.**Figure 2-67.** SO₂ emissions by source category, 1999.

1999, however, total SO₂ emissions have decreased, matching 1995 levels. Again, Table 2-6 explains this increase in terms of Phase I units and Non-Phase I units. Most Phase I plants over-complied in Phase I (1995–1999), banking their SO₂ allowances for use in Phase II, resulting in significant early reductions. However, some Phase I units did increase their emissions during these years, compared to 1995. Since Phase I units account for only 18 percent of the total 1996–1998 increase, the majority of the increase is attributed to those units not yet participating in the Acid Rain Program until Phase II, which began in 2000. When fully implemented, total SO₂ emissions from electric utilities will be capped at 8.95 million tons per year under the Acid Rain Program. For more information on the Acid Rain Program, visit <http://www.epa.gov/airmarkets>. See also Chapter 7, Atmospheric Deposition of Sulfur and Nitrogen Compounds.

National 20-Year Air Quality Trends

The progress in reducing ambient SO₂ concentrations during the past 20 years is shown in Figure 2-68. While there is a slight disconnect in the trend line between 1989 and 1990 due to the mix of trend sites in each 10-year period, an overall downward trend is evident. The national 1999 composite average SO₂ annual mean concentration is 50 percent lower than 1980. In addition to the previously mentioned effects of the Acid Rain Program, these steady reductions over time were accomplished by installing flue-gas control equipment at coal-fired generating plants, reducing emissions from industrial processing facilities such as smelters and sulfuric acid manufacturing plants,

reducing the average sulfur content of fuels burned, and using cleaner fuels in residential and commercial burners.

Regional Air Quality Trends

The map of regional trends in Figure 2-69 shows that ambient SO₂ concentrations are generally higher in the eastern United States. The effects of Phase I of the Acid Rain Program are seen most vividly in the northeast. In particular, concentrations fell 20–25 percent between 1994 and 1995 in EPA Regions 1, 2, 3, and 5. These broad regional trends are not surprising since most of the units affected by Phase I of the Acid Rain Program also are located in the east as shown in Figure 2-70. This figure also shows that ambient concentrations have increased slightly between 1995 and 1997 in Regions 3 and 4 where many of the electric utility units not yet affected by the Acid Rain Program are located.

1999 Air Quality Status

The most recent year of ambient data shows that all counties did meet the primary SO₂ short-term standard, according to Figure 2-71.

Table 2-6. Total SO₂ Emissions from Phase I and Non-Phase I Acid Rain Sources: 1990–1999 (million tons).

	1990***	1995	1996	1997	1998	1999
Phase I (Table I) Units*	8.7	4.455	4.765	4.769	4.66	4.348
Non-Phase I Units**	7.03	7.408	7.749	8.209	8.474	8.104
All Electric Utility Units	15.73	11.863	12.514	12.978	13.134	12.452

* does not include substitution, compensating and opt-in units

** includes substitution, compensating, opt-in and Phase II units

*** Acid Rain phased requirements began in 1995

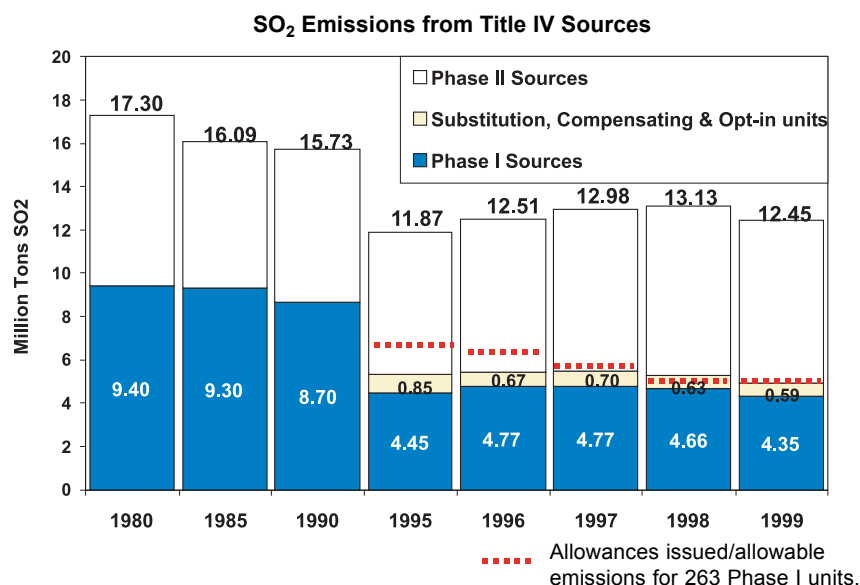


Figure 2-68. Long-term ambient SO₂ trend, 1980–1999.

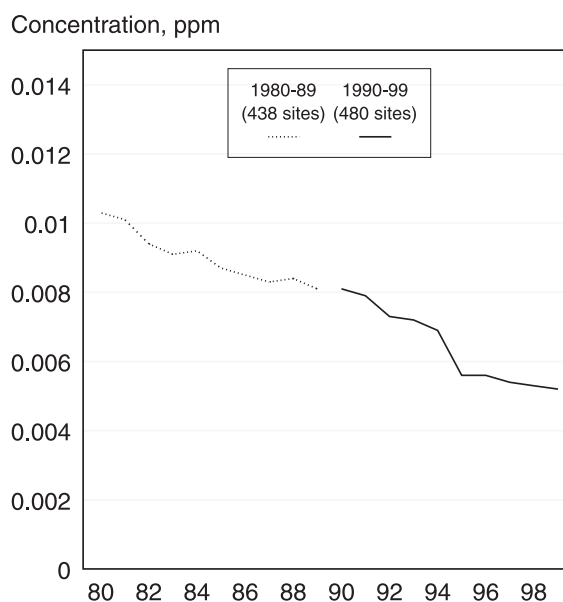
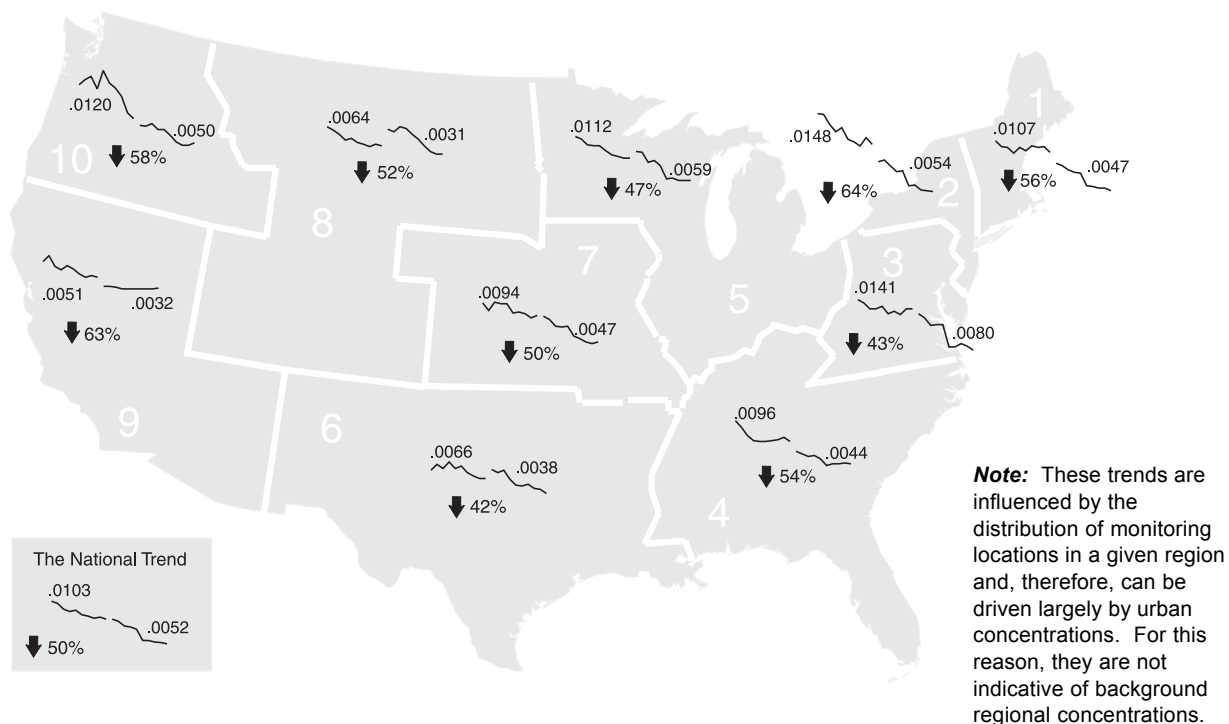


Figure 2-69. Trend in SO₂ annual arithmetic mean concentration by EPA region, 1980–1999.

Alaska is in EPA Region 10; Hawaii, EPA Region 9; and Puerto Rico, EPA Region 2.
Concentrations are ppm.

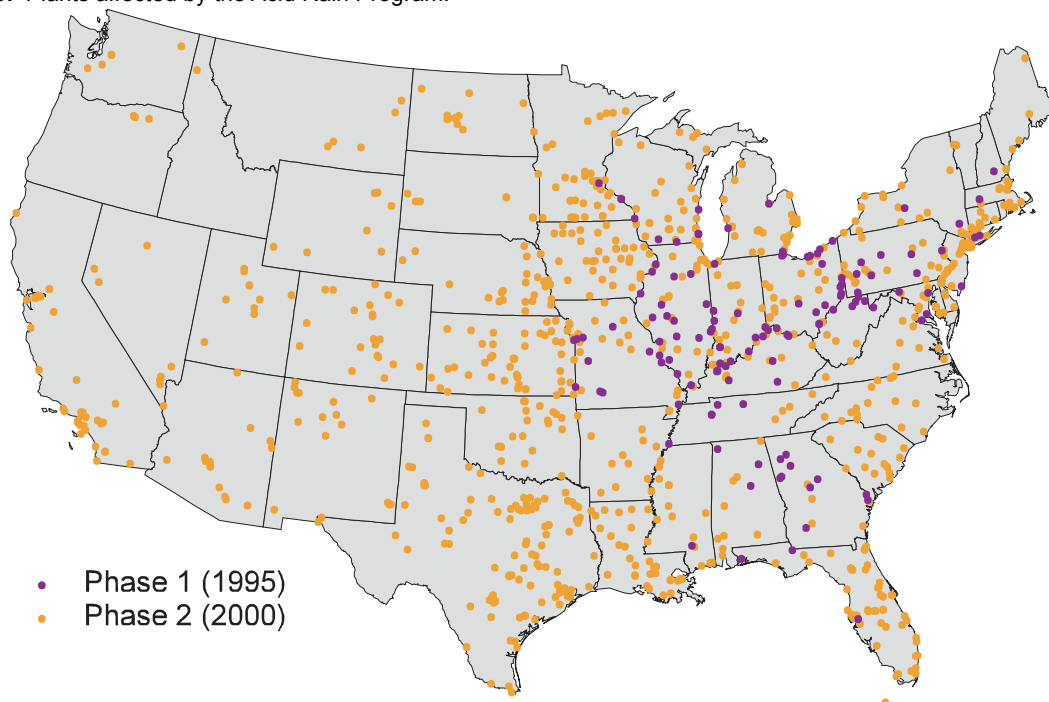
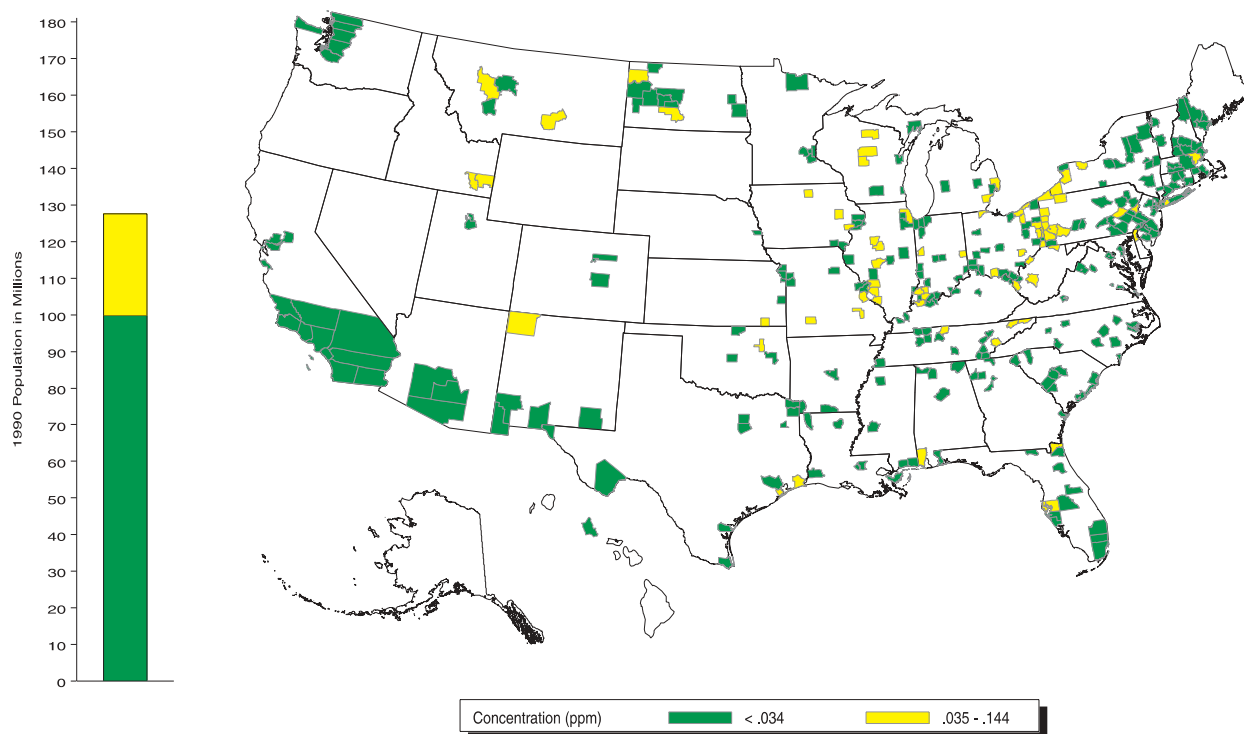
Figure 2-70. Plants affected by the Acid Rain Program.

Figure 2-71. Highest 2nd maximum 24-hour SO₂ concentration by county, 1999.



References

- Note that due to the annual loss and replacement of ambient monitoring sites (e.g., redevelopment, new leases, etc.), too few sites possess a monitoring record sufficient to construct a representative 20-year trend for the nation. Therefore, this report assesses long-term trends by piecing together two separate 10-year trends databases.
- The methods used to estimate CO emissions of some source categories are not consistent in all years over the period between 1980 and 1999. Changes from one method to another make the emissions trend over time appear different than it actually has been. Of particular note is that for 1999, CO emissions from three source categories of open burning are estimated differently than in previous years and show a substantial increase compared to estimates for prior years. These categories of open burning of residential waste, yard waste, and land clearing waste are included in the 'industrial processing' sector of Figure 2-6. The apparent increase in emissions from this sector, and in total CO emissions, from 1998 to 1999 is the result of this change in estimation methodology.
- Oxygenated Gasoline Implementation Guidelines*, EPA, Office of Mobile Sources, Washington, D.C., July 27, 1992.
- Guidelines for Oxygenated Gasoline Credit Programs and Guidelines on Establishment of Control Periods Under Section 211(m) of the Clean Air Act as Amended*, 57 FR 47853 (October 20, 1992).
- Interagency Assessment of Oxygenated Fuels*, National Science and Technology Council, Executive Office of the President, Washington, D.C., June 1997.
- Section 6 of TSCA gives EPA authority to ban, phase out, limit or control the manufacture of any chemical substance deemed to pose an unreasonable risk to the public or the environment. EPA expects to issue a full proposal to ban or phase down MTBE in early 2001.
- "National Ambient Air Quality Standards for Nitrogen Dioxide: Final Decision," *Federal Register*, 61 FR 196, Washington, D.C., October 8, 1996.
- "Review of the National Ambient Air Quality Standards for Nitrogen Oxides: Assessment of Scientific and Technical Information," EPA-452/R-95-005, U.S. Environmental Protection Agency, Research Triangle Park, N.C., September 1995.
- Atmospheric concentrations of NO₂ are determined by indirect photomultiplier measurement of the luminescence produced by a critical reaction of NO with ozone. The measurement of NO₂ is based first on the conversion of NO₂ to NO, and then subsequent detection of NO using this well characterized chemiluminescence technique. This conversion is not specific for NO₂, hence chemiluminescence analyzers are subject to interferences produced by response to other nitrogen containing compounds (e.g., peroxyacetyl nitrate [PAN]) that can be converted to NO). The chemiluminescence technique has been reported to overestimate NO₂ due to these interferences. This is not an issue for compliance since there are no violations of the NO₂ NAAQS. In addition, the interferences are believed to be relatively small in urban areas. The national and regional air quality trends depicted are based primarily on data from monitoring sites in urban locations, and are expected to be reasonable representations of urban NO₂ trends. That is not the case in rural and remote areas, however, where air mass aging could foster greater relative levels of PAN and nitric acid and interfere significantly with the interpretation of NO₂ monitoring data.
- "1998 Compliance Report," U.S. Environmental Protection Agency, Acid Rain Program, Washington, D.C., August 1999.
- "Identification of Ozone Areas Attaining the 1-hour Standard and to Which the 1-hour Standard is No Longer Applicable; Final Rule," *Federal Register*, 63 FR 2804, Washington, D.C., June 5, 1998.
- "Identification of Additional Ozone Areas Attaining the 1-hour Standard and to Which the 1-hour Standard is No Longer Applicable; Final Rule," *Federal Register*, 63 FR 39431, Washington, D.C., July 22, 1998.
- "Identification of Additional Ozone Areas Attaining the 1-hour Standard and to Which the 1-hour Standard is No Longer Applicable; Final Rule," *Federal Register*, 64 FR 30911, Washington, D.C., June 9, 1999.
- "Rescinding Findings that the 1-hour Ozone Standard No Longer Applies to Certain Areas; Final Rule," *Federal Register*, 64 FR 57424, Washington, D.C., November 5, 1999.
- "National Ambient Air Quality Standards for Ozone; Final Rule," *Federal Register*, 62 FR 38856, Washington, D.C., July 18, 1997.
- W.M. Cox and S.H. Chu, "Meteorologically Adjusted Ozone Trends in Urban Areas: A Probabilistic Approach," *Atmospheric Environment*, Vol. 27B, No. 4, Pergamon Press, Great Britain, 1993.
- Currently, 24 of the nation's remaining 31 nonattainment areas for the 1-hour ozone NAAQS are required to operate PAMS sites ("Ambient Air Quality Surveillance: Final Rule," *Federal Register*, 58FR 8452, Washington, D.C., February 12, 1993). Each PAMS network consists of as many as five monitoring stations, depending on the area's population. These stations are carefully located according to meteorology, topography, and relative proximity to emissions sources of VOC and NO_x. As of October 1999, there were 83 active designated PAMS sites.
- "Selected PAMS sites" refers to the inclusion of only those sites with measurements of NO_x or VOCs in both

1995 and 1999. Morning periods for NO_x and VOCs are used because those time frames are generally thought to be an appropriate indicator of anthropogenic emissions.

19. These 24 VOC species are the focus of this analysis because they account for more than 75 percent (by volume) of the VOCs concentrated on in the PAMS program.

20. CASTNet is considered the nation's primary source for atmospheric data to estimate dry acidic deposition and to provide data on rural ozone levels. Used in conjunction with other national monitoring networks, CASTNet is used to determine the effectiveness of national emission control programs. Established in 1987, CASTNet now comprises 79 monitoring stations across the United States. The longest data records are primarily at eastern sites. The majority of the monitoring stations are operated by EPA's Office of Air and Radiation; however, 27 stations are operated by the National Park Service (NPS) in cooperation with EPA. The CASTNet data complement the larger ozone data sets gathered by the State and Local Monitoring (SLAMS) and National Air Monitoring (NAMS) networks with additional rural coverage. A more detailed treatment of CASTNet's atmospheric deposition role and data are provided in Chapter 7: Atmospheric Deposition of Sulfur and Nitrogen Compounds.

21. Similarly, although registering declines in 8-hour ozone levels of 17 and 12 percent respectively over the last 20 years, neither urban nor suburban sites have shown any improvement in ozone concentrations between 1990–1999.

22. This analysis utilizes a non-parametric regression procedure to assess statistical significance a description of which is provided in Chapter 3: Criteria Pollutants – Metropolitan Area Trends.

23. "Volatility Regulations for Gasoline and Alcohol Blends Sold in Calendar

Years 1989 and Beyond," *Federal Register*, 54 FR 11868, Washington, D.C., March 22, 1989.

24. "Reformulated Gasoline: A Major Step Toward Cleaner Air," EPA-420-B-94-004, U.S. Environmental Protection Agency, Office of Air and Radiation, Washington, D.C., September 1994.

25. The Clean Air Act requires that RFG contain 2 percent oxygen by weight. "Requirements for Reformulated Gasoline," *Federal Register*, 59 FR 7716, Washington, D.C., February 16, 1994.

26. The Panel's Executive Summary and final report entitled "*Achieving Clean Air and Clean Water: The Report of the Blue Ribbon Panel on Oxygenates in Gasoline*" can be found at: <http://www.epa.gov/oms/consumer/fuels/oxypanel/blueribb.htm>

27. *National Air Pollutant Emission Trends, 1900-1998*, EPA-454/R-00-002, U.S. Environmental Protection Agency, Research Triangle Park, NC 2000.

28. 1996 PM Criteria Document, <http://www.epa.gov/ttn/oarpg/t1cd.html>.

29. *National Ambient Air Quality Standards for Particulate Matter: Final Rule*, July 18, 1997. (62 FR 38652), http://www.epa.gov/ttn/oarpg/t1/fr_notices/pmnaaqs.pdf.

30. *Revised Requirements for Designation of Reference and Equivalent Methods for PM_{2.5} and Ambient Air Quality Surveillance for Particulate Matter: Final Rule*, July 18, 1997, http://www.epa.gov/ttn/oarpg/t1/fr_notices/pm_mon.pdf.

31. Personal communication with EPA Region 9.

32. Personal communication with EPA Region 3.

33. *National Air Pollutant Emissions Trends, 1900-1998*, EPA-454/R-00-002, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC 27711, March 2000.

34. IMPROVE, Cooperative Center for Research in the Atmosphere, Colorado State University, Ft. Collins, CO, May 2000.

35. *1997 Compliance Report: Acid Rain Program*, EPA-430-R-98-012, U.S. Environmental Protection Agency, Office of Air and Radiation, Washington, D.C., August 1998.